

# Flammability of Epoxy Resins Containing Phosphorus

November 2005

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16. Abstract  As part of a program to develop fire-resistant exterior composite structures for future subsonic commercial and general aviation aircraft, flame-retardant epoxy resins are under investigation. Epoxies and their curing agents (aromatic diamines) containing phosphorus were synthesized and used to prepare epoxy formulations. Phosphorus was incorporated within the backbone of the epoxy resin and not used as an additive. The resulting cured neat epoxy formulations were characterized by thermogravimetric analysis, propane torch test, elemental analysis, microscale combustion calorimetry, and fire calorimetry. Several formulations showed excellent flame retardation with phosphorous contents as low as 1.5% by weight. The fracture toughness and compressive strength of several cured formulations showed no detrimental effect due to phosphorus content. The chemistry and properties of these new epoxy formulations are discussed.					
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## LIST OF ACRONYMS

ASTM	American Standard for Testing and Materials
CFR	Code of Federal Regulations
DDS	4,4'-diaminodiphenylsulphone
DMSO	Dimethyl sulfoxide
DSC	Differential scanning calorimetry
EEW	Epoxy equivalent weights
FAA	Federal Aviation Administration
h	Hours
HOC	Heat of flaming combustion
HPLC/MS	Liquid chromatography/mass spectroscopy
HR	Heat release
HRC	Heat release capacity
HRR	Heat release rate
L	Liter
LOI	Limiting oxygen index
NMR	Nuclear magnetic resonance
OH	Hydroxyl
OSU	Ohio State University
P	Phosphorus
PCFC	Pyrolysis combustion flow calorimetry
phr	Per hundred parts
s	Seconds
SENB	Single-edge notched bend
TGA	Thermogravimetric analysis
TGMDA	Tetraglycidyl-4,4'-methylenedianiline
THF	Tetrahydrofuran

## 1. INTRODUCTION.

The use of composite structures in both commercial and general aviation aircraft has been increasing primarily because of the advantages composites offer over metal (e.g., lower weight, better fatigue performance, no corrosion, better design flexibility, etc.). The new Airbus A380 is expected to have about 22% of the structural weight in composites. About 50% of the structural weight of the new Boeing 787 is proposed to be composites, including for the first time a composite fuselage and wings in a large commercial airliner. Currently, no fire resistance requirements exist for exterior polymer composite structures on airplanes. However, the aircraft manufacturer will be required to demonstrate that polymer structural composites provide equivalent safety to the current material system (aluminum alloy). The primary hazards during aircraft fires are heat, smoke, and toxic gas. In a severe aircraft fire, life-threatening levels of these hazards are produced by cabin flashover, the time to which is largely governed by the rate of heat release of the materials in the fire. Other concerns in a carbon fiber composite fire include the potential release of electrically conductive small carbon fibers that can cause damage to electrical equipment and health problems (from inhalation). However, a study [1 and 2] reported in 1980 concluded that it was unlikely severe damage to electrical equipment would result from an accidental release of carbon fibers from an aircraft fire. Reference 3 discusses the concern about potential health hazards from the exposure to airborne carbon fibers released from a burning airplane containing carbon fiber composite parts. In reference 3, it was concluded, at the present time, that there is no evidence linking airborne carbon fibers to any unusual health hazard.

The use of phosphorus (P) as a flame retardant, particularly in epoxy resins, has been widely studied and is the subject of recent review articles [4-6]. A 3-year BRITE-EURAM Program was conducted in the European community to develop new structural materials with improved fire resistance and reduced smoke and toxicity [7]. This effort concentrated on the use of bis(3-aminophenyl)methylphosphine oxide as a curing agent for epoxies [8, 9, and 10]. Extensive composite evaluation was carried out and several published articles evolved from this work [8, 9, and 10]. Bis(3-aminophenyl)methylphosphine oxide had been used previously as a curing agent for epoxies [11 and 12]. Phosphorus, when incorporated in polymers as an additive or reactive comonomer, is known to impart fire retardation by condensed phase and gas phase mechanisms [9]. In the condensed phase, P catalyzes char formation that protects the underlying material from heat and acts as a barrier to the release of fuel gases from the surface. When acting in the condensed phase as a char catalyst, P retards the spread of fire with minimal release of toxic gases [13]. In the gas phase, P acts as a flame poison with PO species participating in a kinetic mechanism that is analogous to that of halogens in flames [14 and 15]. Gas phase activity is indicated by low heats of flaming combustion, the production of visible smoke and mineral acids (halogens), and high yields of carbon monoxide as consequence of the incomplete combustion of the fuel gases in the flame. Phosphorus has been incorporated into polymeric materials both as an additive and as part of the polymeric chain. Additives are normally more economical but tend to leach out and have a negative impact on processability and mechanical properties. Cured epoxy resins have a high concentration of hydroxyl (OH) groups and, therefore, P-containing flame-retardant compounds are particularly effective because P tends to react with OH groups [4-6 and 8-10].

The intent of this work was to identify reactive organophosphorus compounds that could be incorporated into existing 177°C (350°F) cured epoxy formulations to provide fire-resistant structural composites with little or no compromise in processing, handling, physical, and mechanical properties. The work reported herein concerns the initial research to identify promising epoxide- and amine-functional organophosphorus compounds by screening cured epoxy formulations for flammability and mechanical properties at the laboratory and bench scale.

## 2. EXPERIMENTAL.

### 2.1 MATERIALS.

*N,N,N',N'*-Tetraglycidyl-4,4'-methylenedianiline (TGMDA), 3,4-epoxycyclohexylmethyl -3,4-epoxycyclohexane carboxylate (cycloaliphatic epoxy, Araldite CY 179), and 4,4'-diaminodiphenylsulphone (DDS) were obtained from commercial sources and used as received. Phosphorus oxychloride, phenylphosphonic dichloride, phenyl dichlorophosphate, and triethylamine were purchased from a commercial source and distilled prior to use. All other chemicals were purchased from commercial sources and used without further purification.

### 2.2 CHARACTERIZATION.

<sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P nuclear magnetic resonance (NMR) Spectra were obtained on a Bruker 300 NMR Spectrometer. Differential scanning calorimetry (DSC) was conducted on a Shimadzu DSC-50 thermal analyzer. Melting points were determined by DSC (heating rate of 10°C/min, recorded at the onset and peak of the endotherm). Dynamic thermogravimetric analysis (TGA) was performed on a Seiko 200/220 instrument on cured formulations at a heating rate of 2.5°C/min in nitrogen at a flow rate of 15 cm<sup>3</sup>/min. Char yields were determined by TGA from the mass of the residue remaining at 800°C in nitrogen. Epoxy equivalent weights (EEW) were determined using the hydrogen bromide method [16]. Elemental analyses were performed by Desert Analytics, Tucson, AZ. Liquid chromatography/mass spectroscopy (HPLC/MS) data was collected on a Waters 2695 Separations module interfaced with a Waters Integrity™ System Thermabeam Mass Detector.

### 2.3 SYNTHESIS.

#### 2.3.1 Synthesis of Bis(4-nitrophenyl)methylphosphonate.

A 1-liter (L), 3-neck, round-bottom flask fitted with a mechanical stirrer, an addition funnel, and a condenser was charged with 4-nitrophenol (102.9 g, 0.74 mol), triethylamine (103 mL, 0.74 mol), and tetrahydrofuran (THF, 250 mL). The solution was cooled with an ice water bath. A solution of methylphosphonic dichloride (49 g, 0.37 mol) in 200 mL of THF was added dropwise over a period of 30 minutes. The reaction mixture was stirred overnight and allowed to warm to room temperature. The reaction mixture was poured into 1 L of stirred water and the resulting precipitate was collected by vacuum filtration. The solid was dried in a vacuum oven at 55°C for 4 hours (h) to give 103.86 g (83%) of tan crystalline solid, mp of 120°-122°C (lit. mp 121.5°-122.5°C) [17] by DSC. <sup>1</sup>H NMR dimethyl sulfoxide (DMSO) ppm: [2.05, 2.22] (s, 3H,

methyl), 7.49 (d, 4H), 8.27 (d, 4H).  $^{31}\text{P}$  NMR (DMSO) ppm: 27.4. HPLC/MS: 1 peak,  $m/z$  = 337.

### 2.3.2 Synthesis of Bis(4-aminophenyl)methylphosphonate 1.

A large Parr<sup>TM</sup> bottle was charged with bis(4-nitrophenyl)methylphosphonate (40.32 g, 0.1192 mol), anhydrous methanol (150 mL), and 5% Pd/C (0.2976 g). The bottle was shaken on a hydrogenator for 14 h under 40 psi of  $\text{H}_2$ . The reaction mixture was filtered to remove the catalyst and the filtrate was concentrated to give a yellow oil to which was added 150 mL of isopropanol and a pale yellow solid formed upon standing. The solid was collected and dried in a vacuum oven at 75°C to give 28.6 g (86%), mp of 118-121°C.  $^1\text{H}$  NMR(DMSO) ppm: [1.60, 1.66] (s, 3H, methyl), 5.07 (s, 4H, amine), 6.49 (d, 4H), 6.81 (d, 4H).  $^{31}\text{P}$  NMR (DMSO) ppm: 25.1. HPLC/MS: 1 peak,  $m/z$  = 277.

### 2.3.3 Other Diamines 2 and 3.

Bis(3-aminophenyl)methylphosphine oxide **2** (mp 148-151°C, lit. 146-149°C) [9] and bis(4-aminophenyl)phenylphosphine oxide **3** (mp 264-266°C, lit 264-265°C) [18] were prepared following literature procedures.

### 2.3.4 Synthesis of Diglycidylmethylphosphonate 4.

A 500-mL, three-neck, round-bottom flask fitted with an addition funnel, a mechanical stirrer, and a condenser was charged with glycidol (28.14 g, 0.3762 mol), toluene (200 mL), and triethylamine (38.07 g, 0.3762 mol). The clear solution was cooled with an ice water bath. A solution of methylphosphonic dichloride (23.73 g, 0.1785 mol) in toluene (100 mL) was added dropwise through the addition funnel. The reaction mixture was stirred overnight and allowed to warm to room temperature. The reaction mixture was filtered to remove triethylamine hydrochloride, and the filter cake was washed with 100 mL of toluene. The filtrate was concentrated on a rotary evaporator to give a brown viscous liquid. The liquid was placed under vacuum at 85°C for 1 h with stirring to remove toluene and excess glycidol. (Yield 34.2 g, 87%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) ppm: [1.45, 1.50] (3H, methyl group), [2.56, 2.74] (4H), 3.13 (2H), [3.81, 4.20] (4H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ) ppm: 9.8, 10.2 (methyl), 44.0, 50.0, 65.8.  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ) ppm: 32.5. Anal. Calcd. for  $\text{C}_7\text{H}_{13}\text{O}_5\text{P}$ : C, 40.39%; H, 6.30%; P, 14.88%. Found: C, 39.00%; H, 6.85%; P, 11.98%. (EEW 124, theoretical EEW 104).

### 2.3.5 Other Epoxy Synthesis.

Diglycidylphenylphosphonate **5** (EEW 182, theoretical EEW 135) (Anal. Calcd. for  $\text{C}_{12}\text{H}_{15}\text{O}_5\text{P}$ : C, 53.34; H, 5.60; P, 11.46. Found: C, 52.41; H, 5.30; P, 10.99.) [19], diglycidylphenylphosphate **6** (EEW 198, theoretical EEW 143) [20], triglycidylphosphate **7** (EEW 212, theoretical EEW 83) [21], and triglycidylphosphate **8** (EEW 117, theoretical EEW 89) [22] were prepared following literature procedures.

### 2.3.6 Synthesis of Diethylphenylphosphonate 9.

A 100-mL, round-bottom flask equipped with a magnetic stirrer was charged with ethanol (40 mL, 31.8 g, 0.69 mol) and triethylamine (20 mL, 14.5 g, 0.14 mol). The solution was cooled with an ice water bath. Phenylphosphonic dichloride (10 mL, 13.8 g, 0.07 mol) was added dropwise through an addition funnel. The reaction mixture was stirred for 14 h and then filtered to remove the resulting salt. The filtrate was concentrated on a rotary evaporator to give 13.66 g (91%) of a clear liquid.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) ppm: 1.25 (t, 6H), 4.03 (m, 4H), 7.4 (m, 3H), 7.71 (m, 2H).

## 2.4 CURED NEAT RESIN PLAQUE PREPARATION.

Circular neat resin plaques approximately 4.5 cm in diameter and 0.4 cm thick were prepared by mixing epoxy compounds with 80% of the stoichiometric amount of the curing agent at room temperature. The formulations were heated to and maintained at  $\sim 90^\circ\text{C}$  with periodic stirring for 1-2 h until homogeneous. The formulations were then degassed for 15-20 minutes in a vacuum oven at  $\sim 90^\circ\text{C}$  and subsequently cured for 4 h at  $100^\circ\text{C}$  followed by a 2-h postcure at  $177^\circ\text{C}$ . Except for formulations containing diamine **3**, transparent plaques were obtained.

## 2.5 FLAMMABILITY TESTS.

### 2.5.1 Flame Resistance.

A flame resistance test was conducted by placing a cured epoxy specimen approximately 1.5 by 1.5 by 0.4 cm in a propane torch flame at a  $45^\circ$  angle for 5 or 10 seconds (s) and noting the time required for the sample to self-extinguish upon removal from the flame. Initially, the burn test consisted of placing a piece of the cured resin plaque in the flame of a propane torch for 5 s. As work progressed, the time in the propane torch flame was increased to 10 s. No noticeable difference was detected between 5- and 10-second burns with specimens from the same plaque.

### 2.5.2 Microscale Combustibility.

Five-milligram samples of cured epoxy formulations were heated to  $900^\circ\text{C}$  in a pyrolysis combustion flow calorimeter, at a heating rate of  $1^\circ\text{C/s}$  in a stream of nitrogen flowing at  $80\text{ cm}^3/\text{min}$ . The volatile, anaerobic thermal degradation products in the nitrogen gas stream are mixed with a  $20\text{ cm}^3/\text{min}$  stream of pure oxygen prior to entering a  $1000^\circ\text{C}$  combustion furnace. The heat release rate (HRR)  $dQ/dt$  (W) and sample temperature were measured as a function of time at constant heating rate [23 and 24]. The specific HRR (W/g) is obtained by dividing  $dQ/dt$  at each point in time by the initial sample mass. The heat of combustion of the fuel gases per unit mass of initial sample specific heat release (HR) (J/g) is obtained by time-integration of the specific HRR over the entire test. The char fraction,  $\mu$ , is obtained by weighing the sample before and after the test. A derived quantity, the heat release capacity (HRC) (J/g-K) is obtained by dividing the maximum value of the specific HRR by the heating rate in the test. The HRC is a molecular-level flammability parameter that is a good predictor of flame resistance and fire behavior when only small research sample quantities are available for testing. Three to five samples were tested for each resin formulation. Reproducibility of the test for homogeneous samples is about  $\pm 8\%$ .

### 2.5.3 Ohio State University Rate of Heat Release Test.

Heat release rates in flaming combustion were measured on cured, single-ply, fiberglass-reinforced specimens using a modification of American Society for Testing and Materials (ASTM) E-906 [25], as specified by Title 14 Code of Federal Regulations (CFR) Part 25, Appendix F. In this study, the Ohio State University (OSU) Rate of Heat Release apparatus was modified to measure HRR and total HR by oxygen consumption calorimetry simultaneous with the standard Federal Aviation Administration (FAA) method. A 15- by 15-cm sheet of style 7781 fiberglass was hand impregnated with epoxy formulations containing 0.5 parts per hundred parts (phr) resin of a BF<sub>3</sub>-piperazine catalyst. The resin-impregnated ply was cured in a Carver press under contact pressure for 1 h at 149°C and postcured free standing for 1 h at 177°C. Two specimens were tested per resin formulation.

### 2.5.4 Cone Calorimetry.

A cone calorimeter at 50 kW/m<sup>2</sup> external heat flux was used to test cured neat resin plaques having dimensions of approximate 8.9 by 8.9 by 0.6 cm in flaming combustion. The test was carried out according to a standard procedure ASTM 1354 [26]. Three plaques were tested per resin formulation.

## 2.6 MECHANICAL PROPERTIES.

### 2.6.1 Plane-Strain Fracture Toughness.

Single-edge notched bend (SENB) specimens were tested following ASTM D 5045-99 [27]. Cured epoxy formulations, having dimensions of approximately 1.27 by 6.35 by 0.64 cm, were cut from a neat resin plaque. A crack was initiated with a razor blade [28], and the specimens were tested at a crosshead speed of 0.51 mm/min on a Korros Data test stand equipped with a 0.5-kN (45.5-kg) load cell. Three to five specimens of each resin formulation were tested at room temperature.

### 2.6.2 Compressive Properties.

The compression testing was conducted on cured cylindrical specimens 1.8 cm in diameter by 3.8 cm high using a modification of ASTM D 695 [29]. The test was done on an MTS test stand with a 490-kN load cell. Two extensometers with 2.5-cm gauge lengths were used to measure strain for the modulus calculations. Four specimens of each resin formulation were tested at room temperature.

## 2.7 MOISTURE UPTAKE.

Cured epoxy specimens were dried in a vacuum oven at 100°C for 12 h to a constant weight and then placed in a closed chamber saturated with water vapor at ambient (room) temperature. The specimens were weighed again after 90 days in the moist environment to determine moisture uptake. Three specimens were used per formulation tested.

### 3. RESULTS AND DISCUSSION.

#### 3.1 SYNTHESIS.

The P-containing compounds in this study are known compounds and, where possible, were prepared following literature procedures. The compounds were characterized with  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR, HPLC/MS, elemental analysis, EEW, and melting point where applicable.

##### 3.1.1 Diamines.

Reaction schemes for the synthesis of the organophosphorus diamines are shown in figure 1. Bis(4-aminophenyl)methylphosphonate **1** was prepared by reacting 4-nitrophenol with methylphosphonic dichloride to yield bis(4-nitrophenyl)methylphosphonate that was subsequently reduced to the diamine. Likewise, bis(3-aminophenyl)methylphosphine oxide **2** [12] was prepared through the nitration of diphenylmethylphosphine oxide followed by the reduction of the dinitro compound to the diamine.

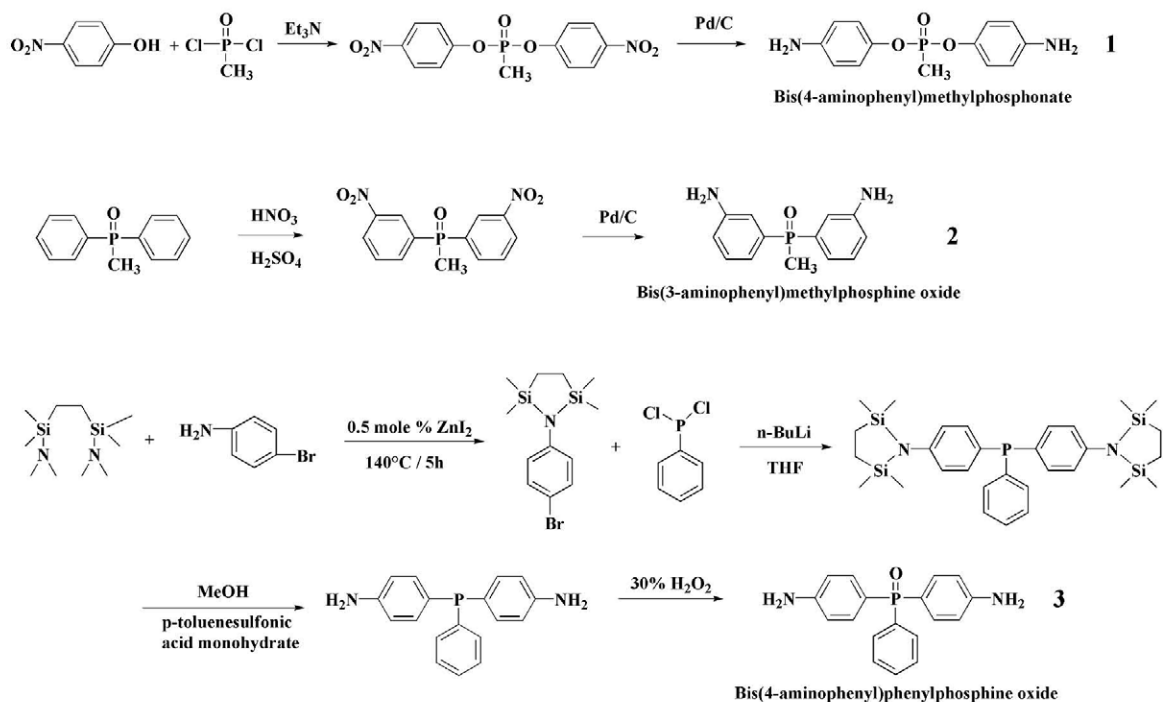


FIGURE 1. PREPARATION OF DIAMINES

Bis(4-aminophenyl)phenylphosphine oxide **3** [30] (mp 264°-266°C, lit. 264°-265°C) [18] was prepared in four steps following literature procedures with an overall yield of 35%: (1) 4-bromoaniline was protected with a STABASE group (1,1,4,4-tetramethyldisilylazacylopentyl) to give 1-bromo-4-(1,1,4,4-tetramethyldisilylazacylopentyl) benzene in 70% overall purified yield [18]; (2) the protected bromoaniline was then reacted with dichlorophenylphosphine in the presence of n-butyl lithium/tetrahydrofuran to give phenylbis[4-(1,1,4,4-tetramethyldisilylazacylopentyl) phenyl]phosphine in 71% yield [18]; (3) the STABASE protecting group was removed in methanol in the presence of *p*-toluenesulfonic acid

monohydrate to give bis(4-aminophenyl)phenylphosphine; and (4) was oxidized with 30% hydrogen peroxide to give bis(4-aminophenyl)phenylphosphine oxide **3** in 75% yield [30].

### 3.1.2 Epoxides.

The organophosphorus epoxy compounds **4-8** were prepared from the reaction of glycidol with the corresponding chlorophosphorus compound (methyl and phenyl phosphonic dichloride, dichlorophenyl phosphate, phosphorus trichloride, and phosphorus oxychloride) in the presence of triethylamine, as shown in figure 2. Epoxy equivalent weights, determined using the hydrogen bromide method, varied significantly from the theoretical values. This is common for epoxies because of impurities such as dimers, trimers, and 1,2-glycols that are present.

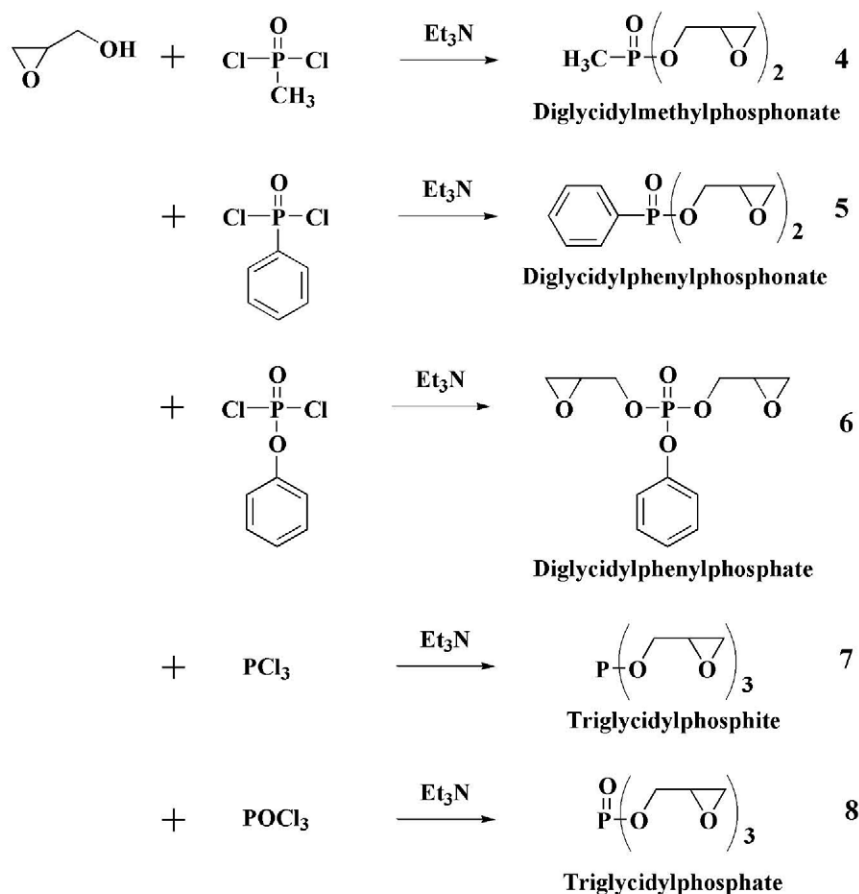


FIGURE 2. PREPARATION OF EPOXY COMPOUNDS

## 3.2 MODEL COMPOUND STUDY OF CHEMICAL REACTIVITY.

Some concern existed about whether the glycidyl functionality could be cleaved at the P-oxygen bond by an amine during curing. To resolve this issue, diethylphenylphosphonate **9** was synthesized to use as a model compound to study this potentially detrimental reaction.

A stoichiometric solution of compound **9** and DDS was stirred at room temperature and subsequently heated. Aliquots were removed after 19 h at room temperature, 2.5 h at  $70^\circ\text{C}$ , 3 h



at 100°C, and 1.5 h at 125°C. The aliquots were analyzed by HPLC and no evidence of reaction between the phosphate ester and the diamine was observed.

### 3.3 CURED NEAT RESIN PLAQUES.

Commercial aerospace structural epoxy formulations contain TGMDA as the base epoxy and DDS as the curing agent and are polymerized (cured) at 177°C. These formulations also generally contain additional components such as a thermoplastic toughening agent, diepoxy, and in some cases, a catalyst. The following formulations are modifications of the commercial aerospace epoxy in which P is introduced at low loading levels (< 5% w/w) using reactive compounds **1-3** and reactive compounds **4-8** as partial replacement for the amine curing agent DDS and epoxy resin TGMDA, respectively. Formulation **F1**, as shown in table 1, is the control (base) formulation in which TGMDA is cured with an 80% stoichiometric amount of DDS to compare properties with the P-containing epoxy formulations. All samples were cured for 4 h at 100°C and postcured for 2 h at 177°C.

TABLE 1. FLAME RESISTANCE OF PHOSPHORUS DIAMINE FORMULATIONS

Formulation	TGMDA (phr)	Diamine Amount	P (%)	Char (% <sup>a</sup> )	Flame Test <sup>b</sup>
<b>F1</b>	100	DDS, 48 phr	0	25	Sustained burn
<b>F2</b>	100	<b>1</b> , 54 phr	3.9	31	Extinguished Immediately
<b>F3</b>	100	<b>2</b> , 47 phr	4.0	23	Extinguished Immediately
<b>F4</b>	100	<b>3</b> , 37 phr	3.7	24	Extinguished Immediately
<b>F5</b>	100	DDS, 36 phr; <b>1</b> , 14 phr	0.9	30	2 s burn
<b>F6</b>	100	DDS, 24 phr; <b>1</b> , 27 phr	1.7	31	Extinguished Immediately

a. Char fraction in nitrogen at 800°C, TGA heating rate 2.5°C/min.

b. Sample placed in propane torch flame for 5 s and removed.

#### 3.3.1 Formulations With Phosphorus-Containing Diamines **F2-F6**.

Formulations **F2-F4** have P-containing diamines **1-3** in place of DDS, respectively, resulting in cured samples having calculated P contents (by weight) of approximately 4.0%. The cured plaques of formulations **F2** and **F3** were transparent, reddish-brown, while **F4** was an opaque yellow. The apparent viscosity of the uncured **F4** formulation was much higher than that observed with the other formulations. Formulations **F5** and **F6** contain a smaller amount of diamine **1** to determine the minimum P content necessary for the specimen to extinguish immediately after removal from the propane torch flame.

#### 3.3.2 Formulations With Phosphorus-Containing Epoxides **F7-F21**.

Epoxy formulations were also prepared where P was introduced via epoxy compounds. These formulations were prepared using only DDS as the curing agent and are listed in table 2. Formulations **F7-F9** contained diglycidylmethylphosphonate **4** in amounts ranging from 10 to

33 phr, as shown in table 2, resulting in cured specimens having P contents ranging from 0.87 to 3.3%. Formulations **F10-F12** were prepared using diglycidylphenylphosphonate **5** in concentrations ranging from 10 to 40 phr. Diglycidylphenylphosphate **6** was used to prepare formulations **F13-F15** with 3.2%, 2.3%, and 1.4% P, respectively. Triglycidylphosphite **7** was also evaluated in cured epoxy formulations. A cycloaliphatic epoxy at a concentration of 20 phr was used as a partial replacement for TGMDA in **F16** and **F17**. This diepoxy is used to help solubilize the DDS, but it is also used in epoxy formulations (generally with boron trifluoride (BF<sub>3</sub>) catalyst) to improve handleability (tack and outtime). However, a BF<sub>3</sub> catalyst was not used in these formulations. Triglycidylphosphite **7** [P(OR)<sub>3</sub>] appeared to be more reactive (advancing cure) than the other P-containing epoxies evaluated in this work. A small amount of gel was observed during the mixing and degassing of the epoxy formulation. This is not unexpected because phosphines [PR<sub>3</sub>] are frequently used as a catalyst in epoxy resins. Formulations **F18-F21** contain triglycidylphosphate **8** with P contents ranging from 0.8% to 3.1%. The cycloaliphatic epoxy mentioned above was not used in these formulations.

TABLE 2. FLAME RESISTANCE OF PHOSPHORUS EPOXY FORMULATIONS

Formulation <sup>a</sup>	TGMDA (phr)	P Epoxy (phr)	P (%)	Char <sup>b</sup> (%)	Flame Test <sup>c</sup>
<b>F7</b>	67	<b>4</b> , 33	3.3	35	Extinguished immediately
<b>F8</b>	80	<b>4</b> , 20	2.1	28	Extinguished immediately
<b>F9</b>	90	<b>4</b> , 10	0.9 <sup>d</sup>	31	2 s burn
<b>F10</b>	60	<b>5</b> , 40	3.2	36	Extinguished immediately
<b>F11</b>	80	<b>5</b> , 20	1.5 <sup>d</sup>	34	Extinguished immediately
<b>F12</b>	90	<b>5</b> , 10	0.8	33	2 s burn
<b>F13</b>	60	<b>6</b> , 40	3.2	44	Extinguished immediately
<b>F14</b>	70	<b>6</b> , 30	2.3	41	Extinguished immediately
<b>F15</b>	80	<b>6</b> , 20	1.4 <sup>d</sup>	37	Extinguished immediately
<b>F16</b>	60 <sup>e</sup>	<b>7</b> , 20	1.6 <sup>d</sup>	35	Extinguished immediately
<b>F17</b>	60 <sup>e</sup>	<b>7</b> , 10	0.9	-	~1 s burn
<b>F18</b>	60	<b>8</b> , 40	3.1	42	Extinguished immediately
<b>F19</b>	70	<b>8</b> , 30	2.4	42	Extinguished immediately
<b>F20</b>	80	<b>8</b> , 20	1.5	37	Extinguished immediately
<b>F21</b>	90	<b>8</b> , 10	0.8	-	~1 s burn

a. Cured with 80% stoichiometric amount of DDS.

b. At 800°C under nitrogen, TGA heating rate 2.5°C/min.

c. Sample placed in propane torch flame for 10 s and removed.

d. Result from elemental analysis.

e. Contains 20 phr cycloaliphatic diepoxy.

### 3.4 MOISTURE UPTAKE.

A study was conducted to determine the moisture uptake of the cured epoxy formulations. Water absorption is known to lower the glass transition temperature and reduce the mechanical properties. The cured resin plaques were first dried in a vacuum oven to remove any absorbed

moisture and subjected to a high humidity atmosphere for 90 days at ambient temperature. As shown in table 3, the baseline material **F1** had an average water uptake of 2.6%, which is similar to commercial 177°C systems. Formulation **F11** containing 20 phr epoxy **5** (phosphonate) had a slightly higher water uptake of 2.9%, while formulation **F20** containing 20 phr epoxy **8** (phosphate) had a water uptake of 4.3%. No firm conclusions can be drawn from this limited data set.

TABLE 3. AVERAGE WATER UPTAKE OF CURED EPOXY FORMULATIONS

Formulation	P (% w/w)	Water Uptake (% w/w)
<b>F1</b>	0	2.6
<b>F11</b>	1.5	2.9
<b>F20</b>	1.6	4.3

### 3.5 NEAT RESIN MECHANICAL PROPERTIES.

Neat resin mechanical properties were determined on several formulations containing P epoxies. Single-edge notched bend specimens were prepared and tested for select formulations to evaluate the effect of incorporating the P-containing compounds on  $K_{Ic}$ . Table 4 lists plane-strain fracture toughness values for selected formulations ranging from 0.47 to 0.79 MPa m<sup>1/2</sup>. The values obtained for formulations **F2**, **F8**, **F11**, and **F20** were essentially the same as measured for **F1** (TGMDA/DDS), while the fracture toughness of **F14** was significantly lower.

TABLE 4. PLANE-STRAIN FRACTURE TOUGHNESS

Formulation	Fracture Toughness (MPa m <sup>1/2</sup> ±1 std. dev.)
<b>F1</b>	0.62 ±0.04
<b>F2</b>	0.68 ±0.04
<b>F8</b>	0.79 ±0.05
<b>F11</b>	0.64 ±0.13
<b>F14</b>	0.47 ±0.09
<b>F20</b>	0.54 ±0.05

Table 5 lists compression moduli formulations containing 20 phr P epoxy (**F11**, **F14**, and **F20**). Compressive moduli ranged from 3.12 to 4.54 GPa for the P-containing epoxies, which is significantly higher than the baseline formulation **F1**. The ultimate compression strength ranged from 188 to 214 MPa. Formulations **F11** and **F20** had compression strengths similar to **F1**, while formulation **F14** was lower. The reduction in fracture toughness observed with **F14** relative to **F1** could exclude epoxy **6** from consideration for use in structural epoxy formulations even though this compound showed a high efficiency in reducing flammability relative to the other P epoxies studied.

TABLE 5. COMPRESSION PROPERTIES OF CURED RESIN FORMULATIONS

Formulation	P (%)	Compression Modulus (GPa)	Ultimate Compressive Strength (MPa)
<b>F1</b>	0	3.12 ±0.02	196 ±14
<b>F11</b>	1.5 <sup>a</sup>	4.54 ±0.06	214 ±4
<b>F14</b>	1.4 <sup>a</sup>	3.50 ±0.03	188 ±2
<b>F20</b>	1.5	4.35 ±0.01	213 ±1

a. Result from Elemental Analysis

### 3.6 CHEMICAL CHARACTERIZATION.

Elemental analysis was performed on cured formulations **F9**, **F11**, **F14**, **F16**, and **F20** to verify the amount of P in the samples. The results are listed in table 6 and show good agreement between found and theoretical values in the cured epoxies. For the samples tested, the % P found by elemental analysis was slightly lower than the amount calculated based on the weight of P-containing epoxy used in the formulation.

TABLE 6. ELEMENTAL ANALYSIS OF SELECTED EPOXY FORMULATIONS AFTER CURING

Formulation	Result	%C	%H	%N	%P
<b>F9</b>	Theoretical	64.84	6.37	7.66	1.01
	Found	64.25	6.13	7.73	0.87
<b>F11</b>	Theoretical	64.59	6.24	7.15	1.59
	Found	61.42	6.39	6.99	1.49
<b>F14</b>	Theoretical	64.20	6.19	7.16	1.49
	Found	62.96	6.24	7.10	1.37
<b>F16</b>	Theoretical	62.36	6.33	6.36	1.65
	Found	60.54	6.48	6.29	1.57
<b>F20</b>	Theoretical	62.02	6.28	6.34	1.57
	Found	61.47	6.62	6.13	1.55

### 3.7 FLAMMABILITY.

#### 3.7.1 Flame Resistance.

The results for flame resistance of the P-containing diamine formulations are presented in table 1. Formulation **F1**, which contained no P, had a char yield of 25% at 800°C in N<sub>2</sub> and exhibited self-sustained burning in air after removal of the flame. Formulations **F2-F4** showed intumescence and extinguished immediately after being removed from the flame with little visible smoke. Formulation **F2**, containing diamine **1** (phosphonate), gave a char yield of 31% at 800°C in N<sub>2</sub>, which is higher than formulations **F3** and **F4** that had char yields similar to the

baseline compound **F1**. Formulation **F5** containing diamine **1** and 0.9% P burned for approximately 2 s after removal from the propane torch flame. Formulation **F6** contained 50% diamine **1**, resulting in a P content of 1.7%. The cured **F6** specimen extinguished immediately after removal from the flame. Char yields at 800°C in N<sub>2</sub> were the same (30%-31%) for all formulations containing diamine **1**.

The results for flame resistance of the P-containing epoxide formulations are presented in table 2. Formulations **F7** and **F8** extinguished immediately upon removal from the propane torch flame, while **F9**, having less than 1% P, burned for approximately 2 s. The three specimens all showed good intumescence and very little visible smoke. A char yield of 35% at 800°C was obtained for specimen **F7**. Both **F10** and **F11**, with 3.2% and 1.6% P content respectively, extinguished immediately upon removal from the propane torch flame and exhibited intumescence and low smoke. Formulation **F12** with 0.8% P burned for approximately 2 s upon removal from the flame but showed good intumescence. As seen with previous specimens, a minimal P content of 1%-1.5% appeared to be necessary to obtain acceptable fire retardation. Char yields at 800°C for formulations **F10-F12** ranged from 33% to 36% and were slightly higher than observed from the corresponding samples containing diglycidylmethylphosphonate **4**. The increased char yields from formulations containing epoxy **5** presumably are from the phenyl ring contributing to the char.

Formulations **F13-F15** extinguished immediately upon removal from the propane torch flame with low smoke and very good intumescence. Char yields for samples containing epoxy **6** at 800°C were higher than observed for formulations containing epoxy **5**. Formulation **F13** had the highest char yield of all the samples tested at 44%. Formulation **F16** containing 1.6% P extinguished immediately after removal from the propane torch flame and showed good intumescence and low smoke. **F17**, which contained less than 1% P, burned for 1 s upon removal from the propane torch flame with moderate intumescence. The char yield of **F16** at 800°C was 35%. Formulations containing epoxy **8** all extinguished immediately except for **F21**, which contained 0.8% P. No increase in char yield was observed between sample **F19** with 2.4% P and **F18** with 3.1% P, suggesting a maximum char yield had been obtained for formulations containing epoxy **8**.

### 3.7.2 Combustibility.

Rapid screening of organophosphorus compounds for combustibility was conducted using pyrolysis combustion flow calorimetry (PCFC). The PCFC uses oxygen consumption calorimetry to measure the rate and amount of heat produced by complete combustion of the fuel gases generated during controlled pyrolysis of a milligram-sized sample. Microscale combustion calorimetry data are shown graphically in figures 3-8. The coefficient of variation for samples **F8**, **F9**, and **F16** taken from the same sample was unusually high at 33%, suggesting inhomogeneity at the 5-mg level of the test specimen. All other samples had coefficient of variation < 5%.

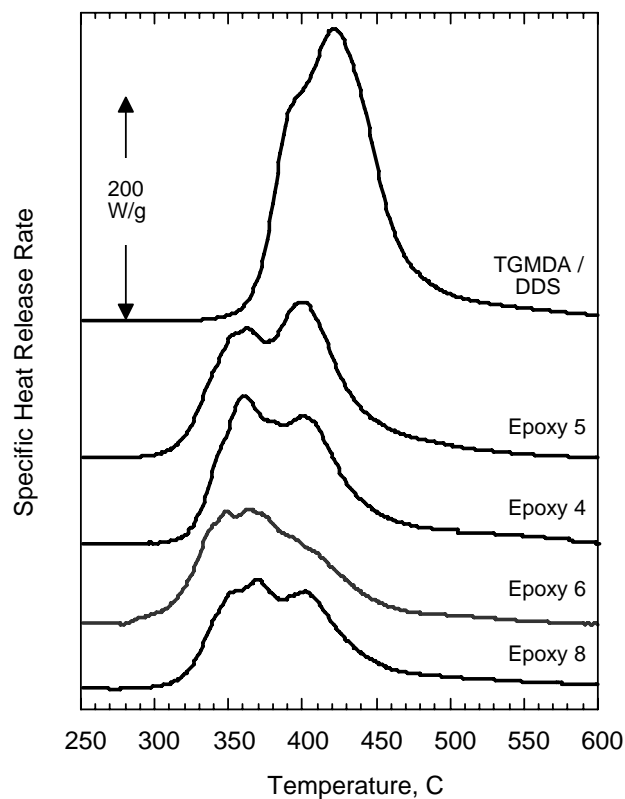


FIGURE 3. SPECIFIC HRR VERSUS TEMPERATURE FOR TGMDA/DDS CONTROL AND EPOXY FORMULATIONS CONTAINING 3% PHOSPHORUS INCORPORATED AS EPOXIDES 4, 5, 6, AND 8

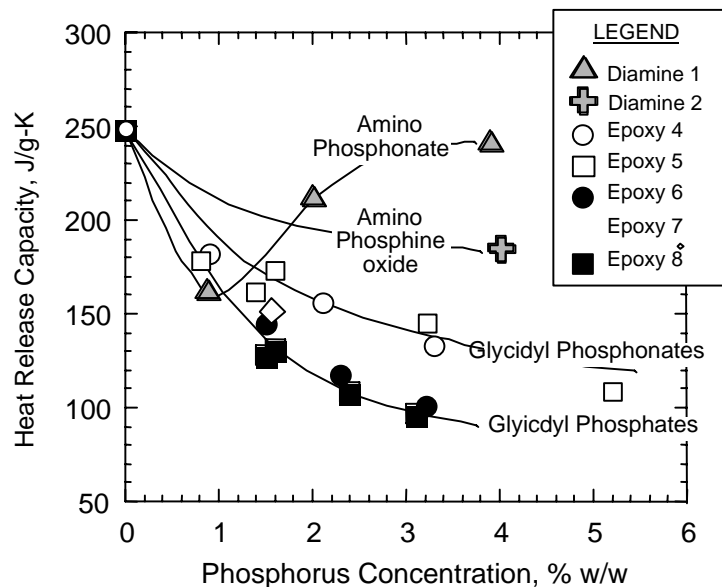


FIGURE 4. HEAT RELEASE CAPACITY VERSUS PHOSPHORUS CONCENTRATION FOR EPOXY FORMULATIONS CONTAINING DIAMINES 1 AND 2 AND EPOXIDES 4, 5, 6, 7, AND 8

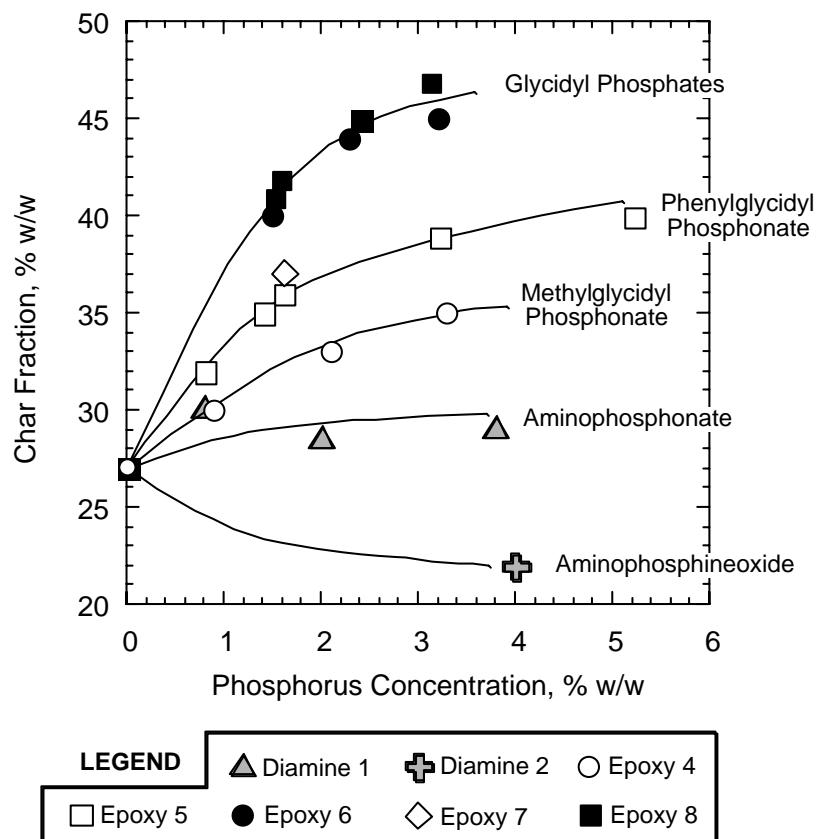


FIGURE 5. ANAEROBIC CHAR FRACTION VERSUS PHOSPHORUS CONCENTRATION FOR EPOXY FORMULATIONS CONTAINING DIAMINES 1 AND 2 AND EPOXIDES 4, 5, 6, 7, AND 8

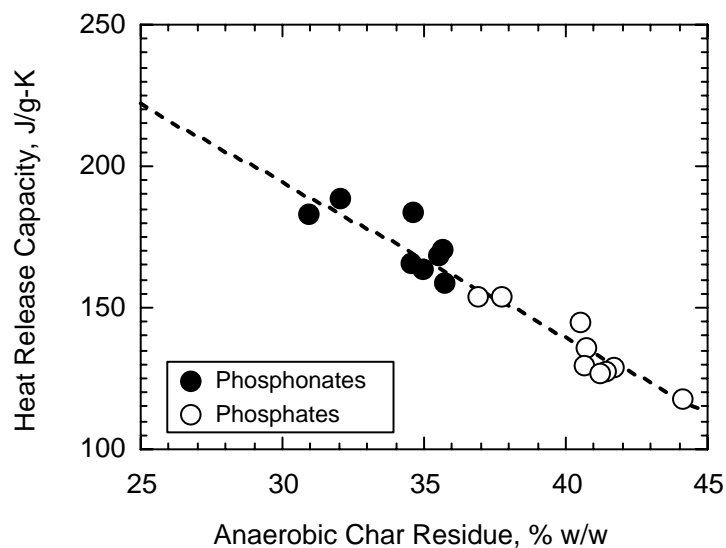


FIGURE 6. HEAT RELEASE CAPACITY VERSUS ANAEROBIC CHAR FRACTION FOR EPOXY FORMULATIONS CONTAINING 1.5% PHOSPHORUS AS EPOXIDES 4, 5, 6, AND 8

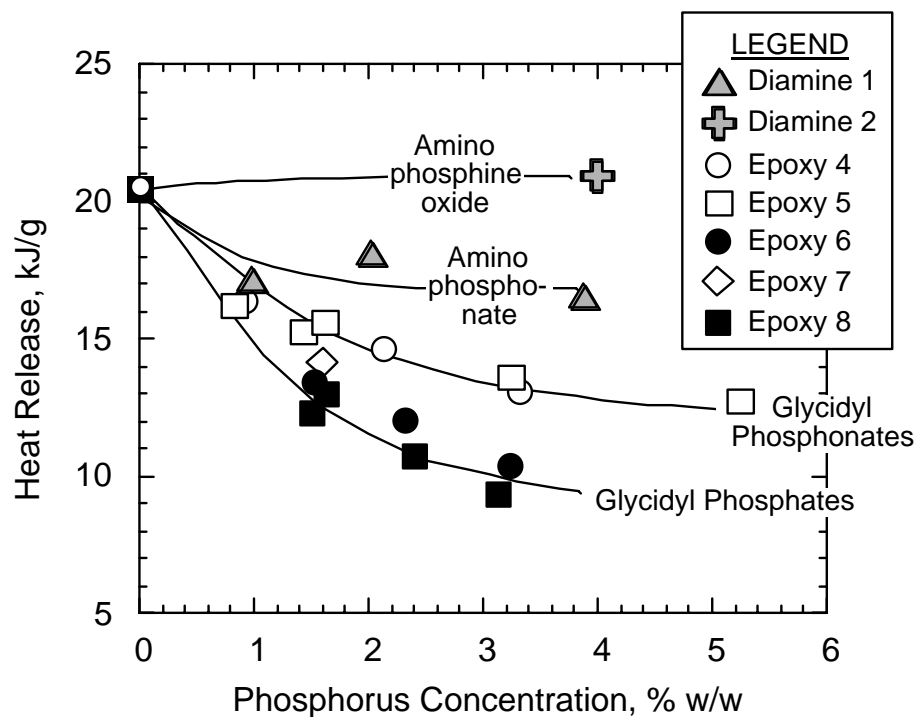


FIGURE 7. HEAT RELEASE VERSUS PHOSPHORUS CONCENTRATION FOR EPOXY FORMULATIONS CONTAINING DIAMINES 1 AND 2 AND EPOXIDES 4, 5, 6, 7, AND 8

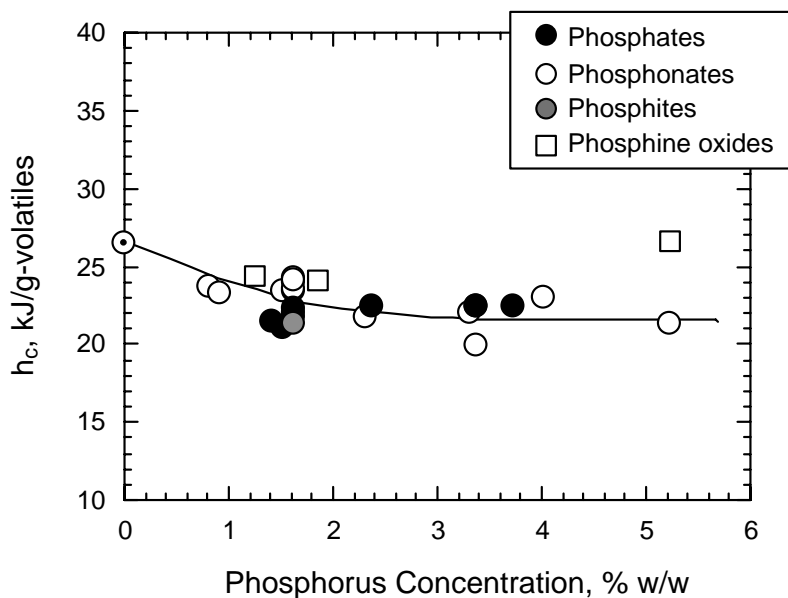


FIGURE 8. HEAT OF COMPLETE COMBUSTION OF VOLATILES VERSUS PHOSPHORUS CONCENTRATION FOR EPOXIDES AND DIAMINES GROUPED BY PHOSPHORUS OXIDE



Figure 3 is a stack plot of specific HRR versus temperature for the TGMDA/DDS control **F1** as well as epoxy formulations **F7** and **F10** containing 3% P incorporated as epoxides **4** and **5**, respectively. Also plotted in figure 3 is the specific HRR data for laboratory formulations containing 3% P incorporated as epoxies **6** and **8**. Each HRR curve is the average of between three and five individual measurements. Curves have been shifted vertically to avoid overlapping data, but the specific HRR scale is unchanged and is indicated by the included arrow. Two HRR peaks are observed for the TGMDA/DDS control, one at 395°C and another at 425°C. The incorporation of 3% P into the polymer backbone as epoxides **4**, **5**, **6**, and **8** shifts these peaks to lower temperatures by about 30°C and reduces the height and area under the curves by a factor of 2. Figure 3 shows that thermal degradation (fuel generation) begins earlier in the heating history for P-containing epoxy formulations but less fuel (combustion heat) is generated over the course of heating.

A two-step thermal degradation process occurring at roughly the same temperatures as indicated in figure 3 for the TGMDA/DDS control has been observed for TGMDA/diglycidylether of bisphenol-A (DGEBA) epoxide mixtures (1:1) cured with diamine **2** [9]. When diamine **2** was used as the curing agent, the decomposition peaks shifted to lower temperatures by roughly the same amount as observed for the HRR peaks of the P-containing epoxies in figure 3. Based on thermal and evolved gas analyses of these systems, it was suggested [9 and 10] that the low temperature process, which is exothermic and involved a large mass loss (60%), was due to dehydration, random scission, and formation of a char precursor. The high-temperature process, which is endothermic and involved less mass loss (20%), was attributed to further decomposition (carbonization) of the char precursor to a thermally stable aromatic structure. These same general processes are probably operative in the present systems. A mechanistic interpretation P-catalyzed charring based on pyrolysis (fuel generation) kinetics [31] is proposed as follows.

The maximum value of the specific HRR for each of the compounds in figure 3 divided by the heating rate in the test (1 K/s) is the HRC of the compound plotted in figure 4. For the compounds in figure 3 containing 3% phosphorus, the HRCs are 260 J/g-K for the TGMDA/DDS control and 140, 130, 100, and 95 J/g-K for the formulations containing epoxides **5**, **4**, **6**, and **8**, respectively (see also figure 4). HRC is related to the decomposition kinetics and combustion parameters of the sample [31 and 32].

$$\text{HRC} = \frac{h_c(1-\mu)}{eRT_p^2/E_a} \approx \frac{h_c(1-\mu)}{\Delta T_p} \quad (1)$$

In equation 1,  $\mu$  is the anaerobic char fraction,  $(1-\mu)$  is the fuel fraction,  $h_c$  (J/g) is the heat of combustion of the fuel gases,  $E_a$  (J/mole) is the activation energy for pyrolysis,  $T_p$  (K) is the temperature at peak mass loss/fuel generation/thermal decomposition rate, and  $e$  and  $R$  are the natural number and gas constant, respectively, and

$$\Delta T_p = \frac{eRT_p^2}{E_a} \quad (2)$$

is the temperature interval over which the majority of pyrolysis (fuel generation) occurs. The data in figure 3 are representative of all the epoxy formulations reported in this report with respect to the temperatures over which heat is released (fuel is generated) during a constant rate of temperature rise. Figure 3 shows that the width of the specific HRR peak at half of the maximum peak height is  $\Delta T_p \approx 80\text{K}$  at  $T_p \approx 410^\circ\text{C}$  (683K) for the TGMDA/DDS control and  $\Delta T_p \approx 100\text{K}$  at  $T_p \approx 380^\circ\text{C}$  (653K) for the epoxy formulations containing 3% P. From these data, a rough estimate of the activation energy for pyrolysis is computed from equation 2,  $E_a = eR(683\text{K})^2/80\text{K} = 132 \text{ kJ/mole}$  for the TGMDA control and  $E_a = eR(653\text{K})^2/100\text{K} = 96 \text{ kJ/mole}$  for the epoxy formulations containing 3% P. Thus, P reduces both the temperature and activation energy for pyrolysis, as would occur for a catalytic mechanism.

Figure 4 shows a plot of HRC versus P concentration for diamines **1** and **2** as well as epoxides **4-8**. Figure 4 shows that the efficiency of P in reducing HRC is glycidyl phosphate > glycidyl phosphite  $\approx$  glycidyl phosphonate > aminophosphonate > aminophosphine oxide. The efficiency of P in reducing HRC is in the same general order as the number of P-O bonds in the starting epoxide or amine compound, i.e.,  $\text{PO}_4 > \text{:PO}_3 \approx \text{RPO}_3 > \text{R}_3\text{PO}$ . The aminophosphonate **1** appears to exhibit anomalous behavior in that HRC shows a minimum at about 1% P and increases at higher P concentration. A flammability minimum at about 2% P was observed in TGMDA/DDS epoxies cured with diamine **2** [9] when tested for limiting oxygen index (LOI) [33], which was attributed to low cross-link density, curing inhibition, or a transition from condensed phase to gas phase activity at high P concentration, the latter being presumably less effective at reducing the LOI. The trends in the data of figure 4 result from variations in the chemical composition and concentration of P-containing epoxies and their effects on HRC.

Figure 5 shows anaerobic char fraction versus P concentration for the P-containing diamines and epoxides as components of a TGMDA/DDS epoxy formulation. Because the TGMDA/DDS is an aromatic, highly cross-linked system, the char fraction is appreciable (27%) even without the addition of P compounds. The efficiency of P in char formation follows the same P-O bond hierarchy observed for HRC, i.e., glycidyl phosphates > glycidyl phosphites  $\approx$  glycidyl phosphonates > aminophosphonates > aminophosphine oxide. A catalytic mechanism of solid-state P activity that is related to the oxide number of the P is indicated by the fact that the additional char mass is several times the mass of P. These data obtained on 5-milligram samples are the molecular-level response of the epoxy formulations to controlled heating and do not reflect the macroscopic effects observed in flame tests or fires in which char may act as a heat or mass transfer barrier (see sections 3.7.1 and 3.7.3).

Figure 6 shows the HRC versus anaerobic char fraction for P-containing epoxies for which the P concentration is  $1.5 \pm 0.2\%$ . It is clear from figure 6 that the anaerobic char fraction  $\mu$  is highly correlated ( $R = 0.93$ ) with combustibility/HRC as per equation 1, and that glycidyl phosphates are more efficient char promoters than glycidyl phosphonates at a particular P concentration (1.5% 1% by weight (w/w) in this figure).

Figure 7 shows specific HR (total heat of complete combustion of volatile fuel per unit original mass of sample) versus P concentration for the diamines and epoxides of this study. The same general ranking is observed for the reduction in HR with regard to P-O bond efficiency, i.e., glycidyl phosphate > glycidyl phosphite  $\approx$  glycidyl phosphonate > aminophosphonate >

aminophosphine oxide. Although the amount of heat generated per unit mass of epoxy by combustion of the fuel gases decreases with increasing P concentration, this is primarily the result of a reduction in the fuel fraction rather than the heat of combustion of the volatiles ( $h_c$  in equation 1). The heat of combustion of the volatiles was calculated as  $h_c = HR/(1-\mu)$  from the data in figure 7 (HR) and the data in figure 5 ( $\mu$ ) for all the samples tested for combustibility. Figure 8 shows the results of these calculations as  $h_c$  versus P concentration grouped by P compound. The slight reduction in  $h_c$  may be associated with P but it is independent of P concentration above 1.5% w/w. All the data falls within the relatively narrow range  $h_c = 23.2 \pm 1.8$  kJ/g with no systematic variation related to chemical composition of the P-containing compound or the anaerobic char fraction.

### 3.7.3 Fire Behavior.

Average peak HRR and average HR at 2 minutes, according to 14 CFR Part 25, Appendix F, are reported in table 7 for selected specimens. The FAA-allowable values are a peak HRR of 65 kW/m<sup>2</sup> over a 5-minute test and 65 kW-min/m<sup>2</sup> total HR at 2 minutes. HRR requirements for exterior composites did not exist at the time of this writing. This test procedure is used to certify large-area components in the passenger compartment of a commercial airplane. The OSU test was carried out for screening purposes only. Formulation **G1**, which contained no P, has an average peak HRR of 97 kW/m<sup>2</sup> that is well above the FAA-allowable value. Specimens **G2-G3** contain epoxy **5** with P contents ranging from 1.5% to 3.4%. **G2** (1.5% P) and **G3** (3.4% P) show lower peak HRR relative to **G1** of 72 kW/m<sup>2</sup> and 51 kW/m<sup>2</sup>, respectively. Specimens **G4** and **G5** contain epoxy **8** with P contents of 1.6% and 3.4%, respectively. The HRR values for these two specimens were similar at 65 kW/m<sup>2</sup> and 63 kW/m<sup>2</sup>. The results show that flaming HRR of TGMDA/DDS epoxy is reduced by approximately the same factor as HRC (see figure 4) when P is incorporated at the levels examined. The single-ply specimens tested in the OSU fire calorimeter are thin and burn quickly to completion so that charring has little effect beyond reducing the fuel fraction as per the combustibility test (see 2.5.2). Thicker specimens provide sufficient mass for copious char formation that can act as a barrier to heat and mass transfer.

TABLE 7. OHIO STATE UNIVERSITY TEST RESULTS ON SINGLE CURED EPOXY GLASS PLY<sup>a</sup>

Formulation <sup>b</sup>	TGMDA phr	P-epoxy phr	P (%)	Average Peak HRR, kW/m <sup>2</sup>	Average HR (2-min) kW-min/m <sup>2</sup>
<b>G1</b>	100	-	0	97	29
<b>G2</b>	80	<b>5</b> , 20	1.5	72	21
<b>G3</b>	60	<b>5</b> , 40	3.4	51	15
<b>G4</b>	80	<b>8</b> , 20	1.6	65	18
<b>G5</b>	60	<b>8</b> , 40	3.4	63	14

a. Cured with 80% stoichiometric amount of DDS

b. Contain 0.5 phr BF<sub>3</sub>-piperazine

Figure 9 shows cone calorimeter data for 6-mm-thick samples of **F1**, **F11**, and **F20** tested at an external heat flux of 50 kW/m<sup>2</sup> according to standard methods [27]. Intumescence began

immediately after ignition of formulations **F11** and **F20** containing 1.5% P as epoxides **5** and **8**, producing a voluminous char that reduced the HRR to near zero for 1-2 minutes into the test. In contrast, very little intumescence was observed for the TGMDA/DDS control, **F1**. The intumescent char layer on **F11** and **F20** bursts open at 150 and 220 s, respectively, releasing trapped fuel gases in a violent deflagration. This intumescence at 1.5% P is probably responsible for the ignition resistance to a brief (10 s) flame exposure shown in tables 1 and 2.

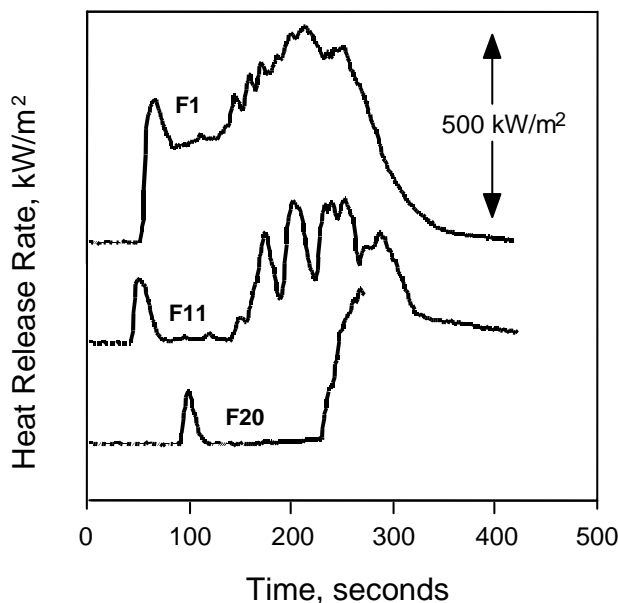


FIGURE 9. FIRE (CONE) CALORIMETER DATA AT 50 kW/m<sup>2</sup> EXTERNAL HEAT FLUX FOR FORMULATIONS F1 (TGMDA/DDS CONTROL), F11 (1.5% P), AND F20 (1.5% P) (Complete suppression of HRR is observed for F11 and F20 for 1-2 minutes after ignition.)

The total integrated HRR obtained from oxygen consumption measurements made during the fire calorimetry tests (OSU and cone) is the effective heat of flaming combustion (HOC). Flaming combustion is never completely (100%) efficient due to the finite residence time of the fuel/air mixture in the combustion zone of the flame, which leads to soot formation and incomplete combustion products such as carbon monoxide and unburned hydrocarbons. Combustion is less efficient when gas-phase-active flame retardants are released into the flame during burning. The efficiency of flaming combustion  $\chi$  is calculated by dividing the effective HOC by the heat of complete combustion of the volatiles from the microcalorimeter tests of the same formulation, i.e.,  $\chi = \text{HOC}/h_c$ . If P is released from the epoxy during burning and enters the gas phase to inhibit combustion in the flame, then the flaming combustion efficiency should decrease when P is present. The average effective HOC from 40 individual tests of epoxy formulations over a range of P concentration from 0%-5% w/w in flaming combustion was  $\text{HOC} = 16.4 \pm 2.4$  kJ/g. The heat of complete combustion obtained from microcalorimeter tests of the same 40 formulations is  $h_c = 23.2 \pm 1.8$  kJ/g, with no systematic variation with chemical composition of the P compound. Consequently, the average combustion efficiency for TGDDM/DDS epoxy formulations containing 0%-5% w/w P is  $\chi = \text{HOC}/h_c = (16.4 \pm 2.4 \text{ kJ/g})/(23.2 \pm 1.8 \text{ kJ/g}) = 0.7 \pm 0.1$ . The individual data are shown in figure 10 and identified by P-compound as phosphates

(open circles), phosphonates (solid circles), or not applicable (e.g., TGMDA/DDS) or not available (N/A) at the time of this writing (grey circles). A flaming combustion efficiency of 70% ( $\chi = 0.7$ ) is typical of polymers that generate significant smoke during burning, as was the case for these epoxies. There is no discernable effect of P concentration in the solid on the combustion efficiency in the flame within the error of the measurements and calculation indicated by dashed lines in figure 10. This data supports the conclusion that P incorporated as P-containing epoxides and diamines (figures 5, 6, 8, 9, and 10) acts primarily in the condensed phase by promoting char formation. Phosphorus is highly efficient in this regard, as the mass of char produced is several times the mass of P incorporated into the polymer. The effect of char at the molecular level is to reduce the amount of combustible fuel.

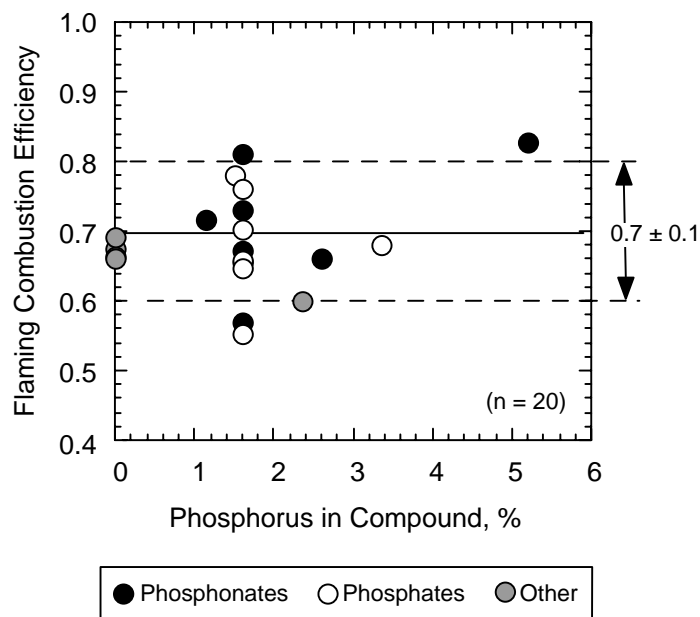


FIGURE 10. FLAMING COMBUSTION EFFICIENCY VERSUS PHOSPHORUS CONCENTRATION FOR TGMDA/DDS CONTROL AND EPOXY FORMULATIONS CONTAINING EPOXIDES 4, 5, 6, AND 8

#### 4. SUMMARY.

Phosphorus-containing epoxy formulations were studied as part of a program to develop technology leading to fire-retardant exterior structural composite resins. Phosphorus was introduced as either part of the diamine curing agent or part of an epoxy compound in a typical aerospace epoxy, TGMDA/DDS. The diamines included both phosphonate and phosphine oxide structures while the epoxide compounds included phosphates, phosphite, and phosphonates.

Flame resistance, microscale combustibility, and fire behavior were used to assess flammability of P-containing epoxy and diamine formulations. Improved flame resistance is observed at a P concentration of 1.5% by weight, while fire resistance is observed at P concentration of about 3% by weight, above which TGMDA/DDS epoxies pass the FAA HRR test for large-area aircraft cabin interior components.

Flaming combustion efficiency was used as a global measure of gas phase activity but did not indicate that P had any significant effect on flame chemistry for the compounds studied. Instead, flammability reduction was attributed to the promotion of charring by P in the condensed phase. Phosphorus appears to act as a catalyst for char formation, i.e., P promotes char but is not consumed in the chemical reactions that form char. Catalytic activity is indicated by (1) the several-fold increase in char mass per unit mass of incorporated P; (2) lowering of the temperature and activation energy for thermal decomposition; and (3) saturation of charring at higher P loadings, typically > 3%. The activity of P as a char catalyst is in the same order as the number of P-O bonds in the diamine or epoxide, i.e., organophosphate ( $\text{PO}_4$ ) > organophosphite ( $:\text{PO}_3$ )  $\approx$  organophosphonate ( $\text{RPO}_3$ ) > organophosphine oxide ( $\text{R}_3\text{PO}$ ). This hierarchy could indicate that the active catalyst for char formation is a P oxide or P acid.

Phosphorus incorporated as a reactive component (diamine or glycidylether) into a TGMDA/DDS aerospace epoxy at an effective level for flame resistance ( $\sim 1.5\%$  P) has no effect on fracture toughness, compressive strength, or compressive modulus with the exception of diglycidylphenylphosphate, which had lower fracture toughness.

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